Electronic Supporting Information (ESI)

Helically Twistable Cyanoacrylate Crystal with Simultaneous Photomechanical Bending

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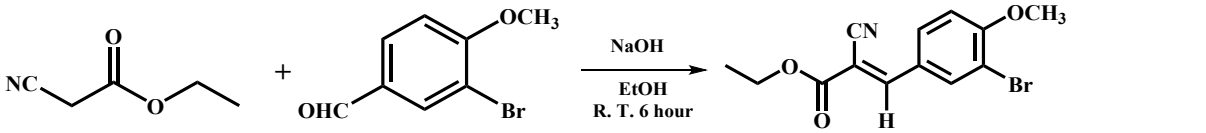
Table of Contents:

1. Materials

The compounds ethyl 2-cyanoacetate and 3-bromo-4-methoxy benzaldehyde were purchased from Spectrochem and BLDpharm for synthesis purposes. Commercially available solvents were used as received without further purification for crystallization.

2. Synthesis procedure of compound ECA.

Compound **ECA** was synthesized following a reported procedure by dissolving 3-bromo-4-methoxy benzaldehyde in a 100 ml round-bottom flask containing 15 ml of ethanol, after which NaOH was added and to the resultant solution ethyl 2-cyanoacetate (1 mmol) was added slowly.[1] The mixture was stirred for 6 hours at room temperature, and after 6 hours, the product was precipitated out from the reaction medium. The progress of the reaction was checked periodically using TLC. The obtained precipitate was filtered out and dried off with a decent yield of ~75%. Crystallization was done by the slow evaporation technique at room temperature, and single crystals were obtained from hot solvents such as methanol/acetonitrile in a 1:1 ratio. Well-diffraction quality crystals appeared from crystallization vessel three days later.



ethyl 2-cyanoacetate | 3-bromo-4-methoxy benzaldehyde | ethyl (*E*)-3-(3-bromo-4-methoxyphenyl)-2-cyanoacrylate

Scheme 1. Synthesis procedure of compound **ECA.**

3. Experimental Section

3.1 NMR spectroscopy studies: ^{1}H NMR spectra were recorded using a Bruker Avance Onebay 400 MHz. The DMSO-D_6 solvent system was used to record the spectra. ^{1}H NMR spectra were collected under standard conditions. Chemical shifts (δ) are reported in parts per million (ppm).

3.2 Single crystal X-ray diffraction: Single crystal data of **ECA** was collected on a Bruker D8 Venture system with graphite monochromatic (Mo Kα, 0.71073 Å) radiation at 200 K. Data reduction was performed using the Bruker AXS SAINT and SADABS programs. The structures were solved by direct methods using SHELXT 2018, followed by successive Fourier and difference Fourier transformations.[2] SHELXL 2013 was used for full-matrix least-squares refinements on F^2.[3] Refinement of coordinates and anisotropic thermal parameters of nonhydrogen atoms was performed using the full-matrix least-squares method. Mercury software was utilized for molecular representations in the ORTEP diagrams. Although the crystal structure of crystal **ECA** has been reported previously,[4] we have successfully reproduced the same structure as part of our study. Detailed data collection, structure refinement, and crystallographic data are shown in **Table S2**, ESI.

3.3 Powder X-ray diffraction studies: Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D8 Advance diffractometer equipped with Cu Kα radiation = 1.540 Å. The powdered samples were dried and then analyzed over a 2θ range of 5–50°, with a step size of 0.02°. Before data collection, the instrument was calibrated using a silicon standard. The X-ray tube was operated at a voltage of 40 kV and a current of 50 mA respectively.

3.4 Differential scanning calorimetry: Differential scanning calorimetry (DSC) analysis was performed using a Mettler Toledo DSC 822e instrument to measure enthalpy changes. The

dried crystals were placed in a 40 μL aluminum pan and securely crimped. The sample was then heated from room temperature (25 °C) to 200 °C at a heating rate of 10 °C min^{-1}, with an empty aluminum pan serving as the reference. Nitrogen gas was used as the purge gas at a flow rate of 40 mL min^{-1}.

3.5 Field emission scanning electron microscopy: Field Emission Scanning Electron Microscopy (FE-SEM) analysis was performed using an FEI NOVA NANO 450 instrument at an accelerating voltage of 20 kV to achieve ultra-high resolution. The imaging was conducted with a dwell time of 6–10 μs across various magnifications, covering an area range of 200 to 5 μm.

3.6 Raman Spectra of Pristine, Twisted and Untwisted Crystal: Raman spectra were recorded for straight, twisted, and untwisted forms of Crystal **ECA** using a confocal Raman microscope (TechnoS IndiRAM CTR 500C Micro Raman Spectrometer, India) equipped with a CCD detector. A 532 nm diode laser served as the excitation source. For the straight crystals, a 50× objective lens was used, with spectra collected at an 8-second integration time and averaged over 5 accumulations. For the twisted and untwisted regions, measurements were also taken using the same 50× lens (laser beam diameter: 1 μm), with identical acquisition parameters (8-second integration, 5 accumulations).

3.7 Solid-state UV visible studies: The crystals of **ECA** were gently ground using mortar and pestle and solid-state UV-visible spectral analysis was done using SHIMADZU UV-Visible NIR spectrophotometer (Model: UV 3600PLUS).

3.8 Solid-state Photoluminescence spectroscopy studies: The crystals **ECA** were gently ground using mortar and pestle and approximately 20 – 50 mg of the ground sample were taken for solid-state photoluminescence analysis using Edinburgh Fluorescence spectrometer, UK (Model: FLS 1000)

Table S1: Results from the crystallization of compounds ECA from one solvent or mixture of solvents.

5 mg of **ECA** (approx. 0.018 mmol) was dissolved in a 1:1 (v/v) mixture of methanol (AR grade, 5 mL) and acetonitrile (HPLC grade, 5 mL) yielding a solution with a concentration of 1.8 mM, in a 50 mL beaker, followed by slow evaporation through a perforated aluminium foil cover.

S.No.	Solvents	Compound ECA
1.	Ethyl Acetate + n-Hexane (1:1)	Powder
2.	Dichloromethane + Methanol (1:1)	Powder
3.	Ethyl Acetate + Methanol (1:1)	Powder
4.	Methanol	Needles
5.	Acetonitrile	Needles
6.	Methanol + Acetonitrile (1:1)	Fine needles
7.	Chloroform	Powder

Table S2: Crystallographic Information Table of Crystal ECA.

Compound	**Crystal ECA**
Formula	$C_{13}H_{12}BrNO_3$
Molecular weight	310.15
T/K	200
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.562(7)
b (Å)	4.0956(2)
c (Å)	27.5269(15)
α (°)	90
β (°)	95.943(2)
γ (°)	90
Volume/Å^3	1296.48(12)
Z	4
ρ, mg.cm^{-3}	1.589
μ /mm^{-1}	3.170
Reflections collected	19873
Independent Reflections	3231
R_{int}	0.099
Goodness-of fit	1.131
Final R[I>2σ]	0.0348
R_1	0.0818
wR_2	0.0961
CCDC Number	**2528375**

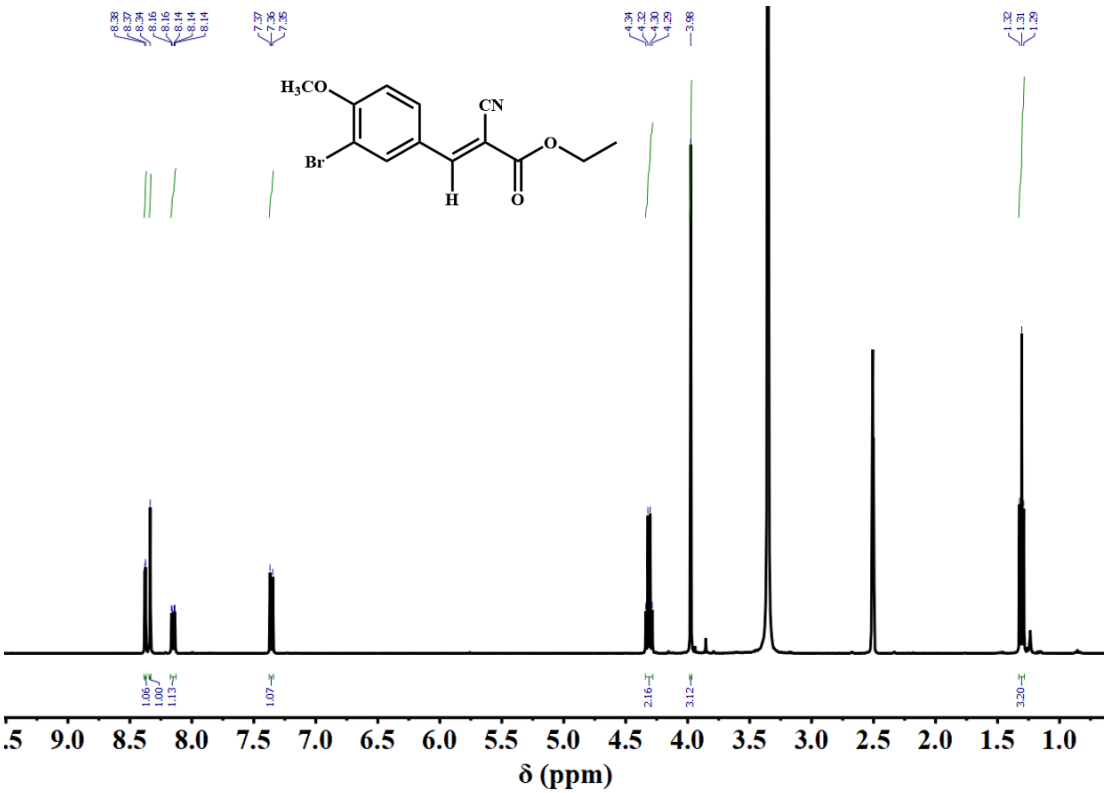


Fig. S1 [1]H NMR spectrum of Crystal **ECA** (solvent: DMSO-d6, peak at 2.51 ppm).

Crystal **ECA**: [1]H NMR (400 MHz, DMSO-d6) δ 8.38 (d, J = 2.2 Hz, 1H), 8.34 (s, 1H), 8.18 – 8.12 (m, 1H), 7.36 (d, J = 8.8 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 3.98 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H).

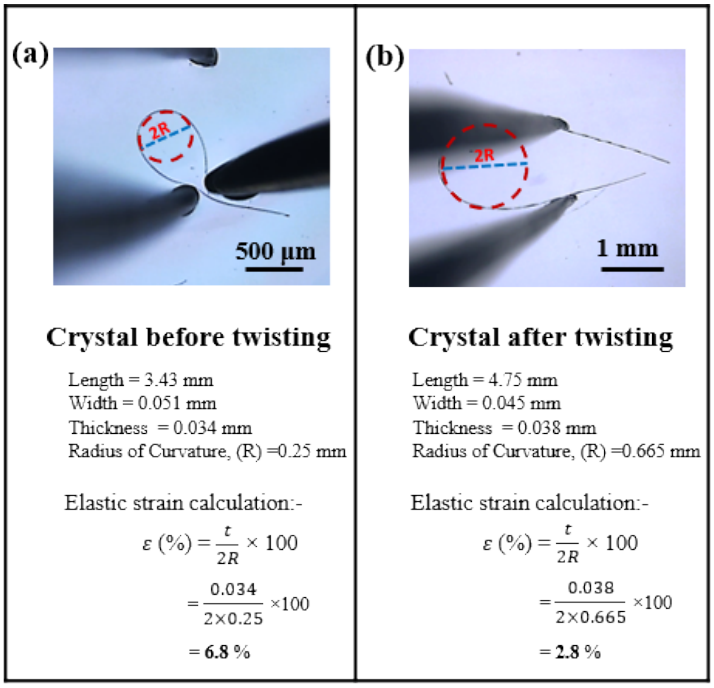


Fig. S2 Elastic strain calculation of the crystals before twisting (a) and after twisting (b).

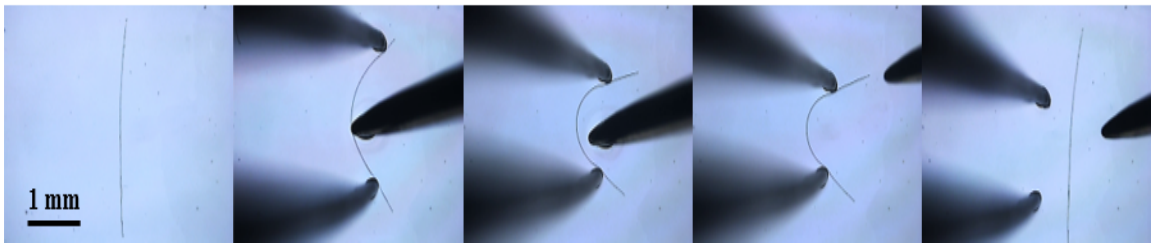


Fig. S3 Stepwise elastic bending cycles of crystal **ECA** before twisting.

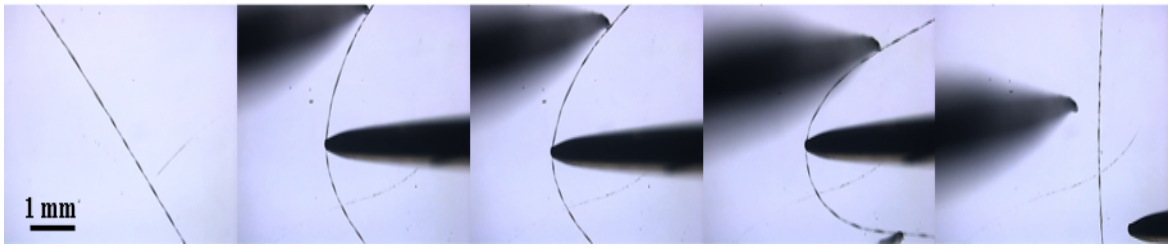


Fig. S4 Stepwise elastic bending cycles of crystal **ECA** after twisting.

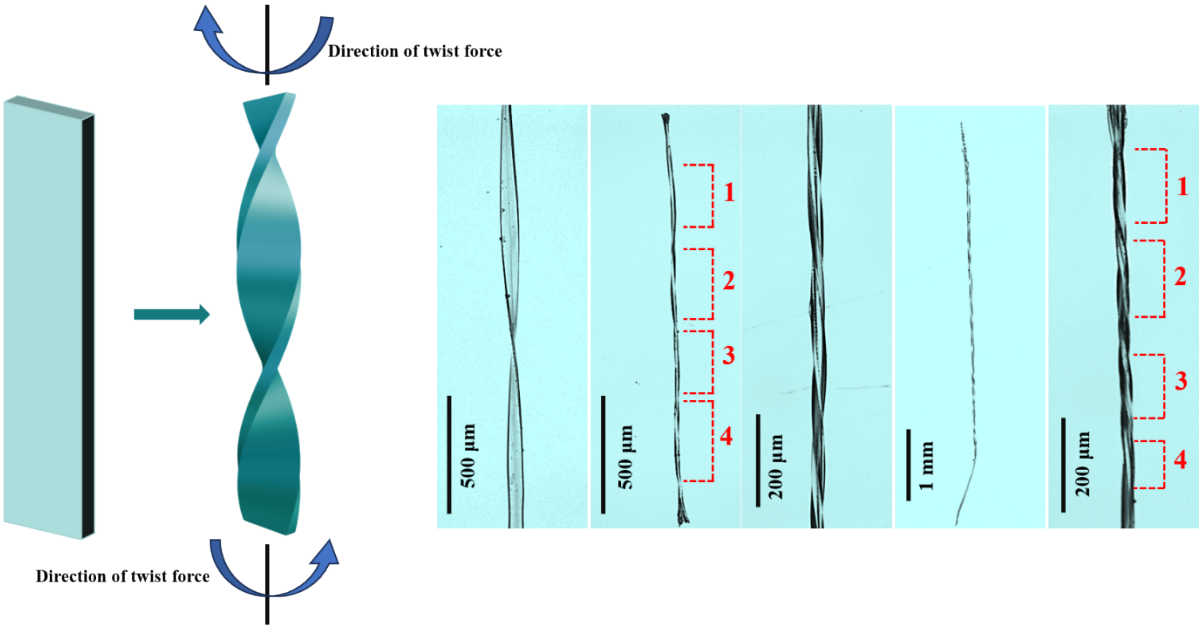


Fig. S5 Shows minimum and maximum number of pitches by applying the controlled twisting force on the crystal **ECA**.

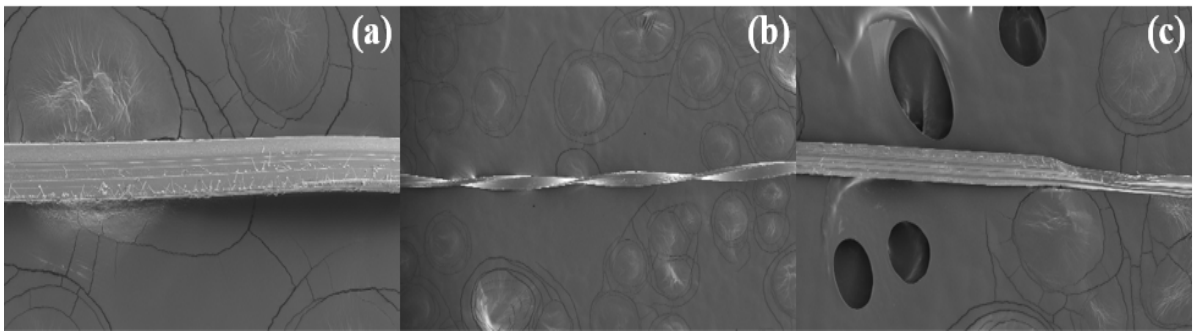


Fig. S6 FESEM images of crystal **ECA**: straight crystal (a), twisted crystal (b) and untwisted crystal (c).

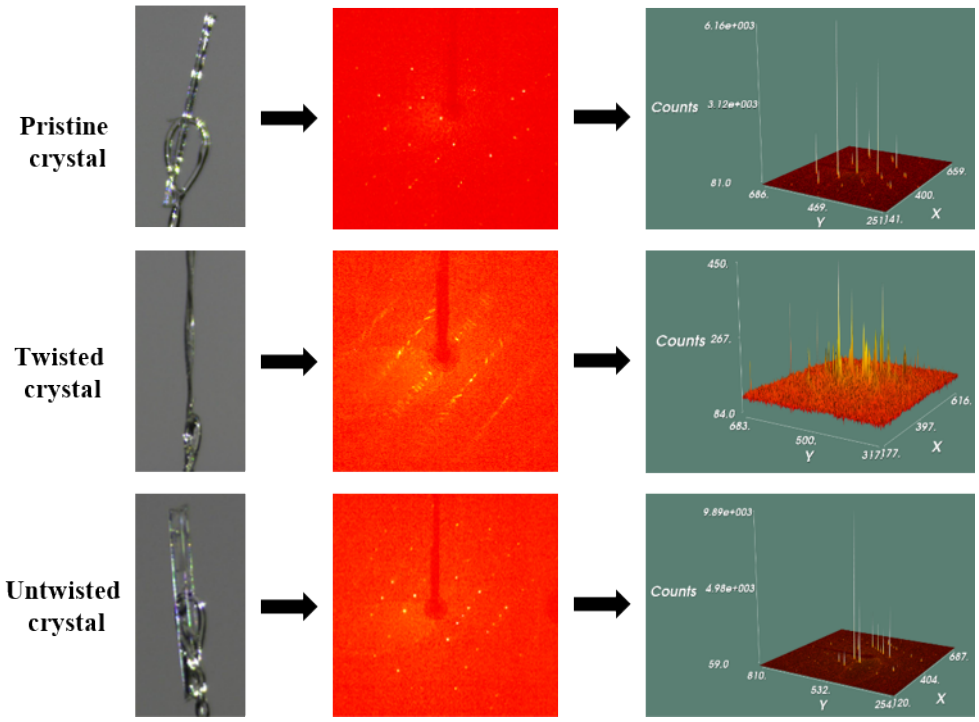


Fig. S7 Representative single crystal X-ray diffraction frames for a pristine, twisted and untwisted crystal of Crystal **ECA.**

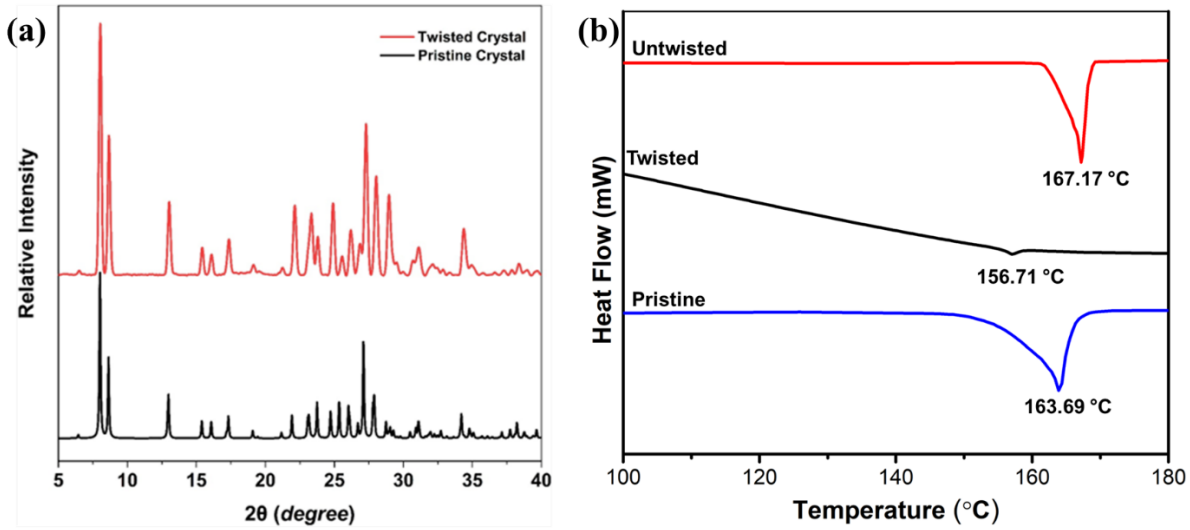


Fig. S8 (a) and (b) shows PXRD profile and DSC profile of pristine, twisted and untwisted crystal **ECA**.

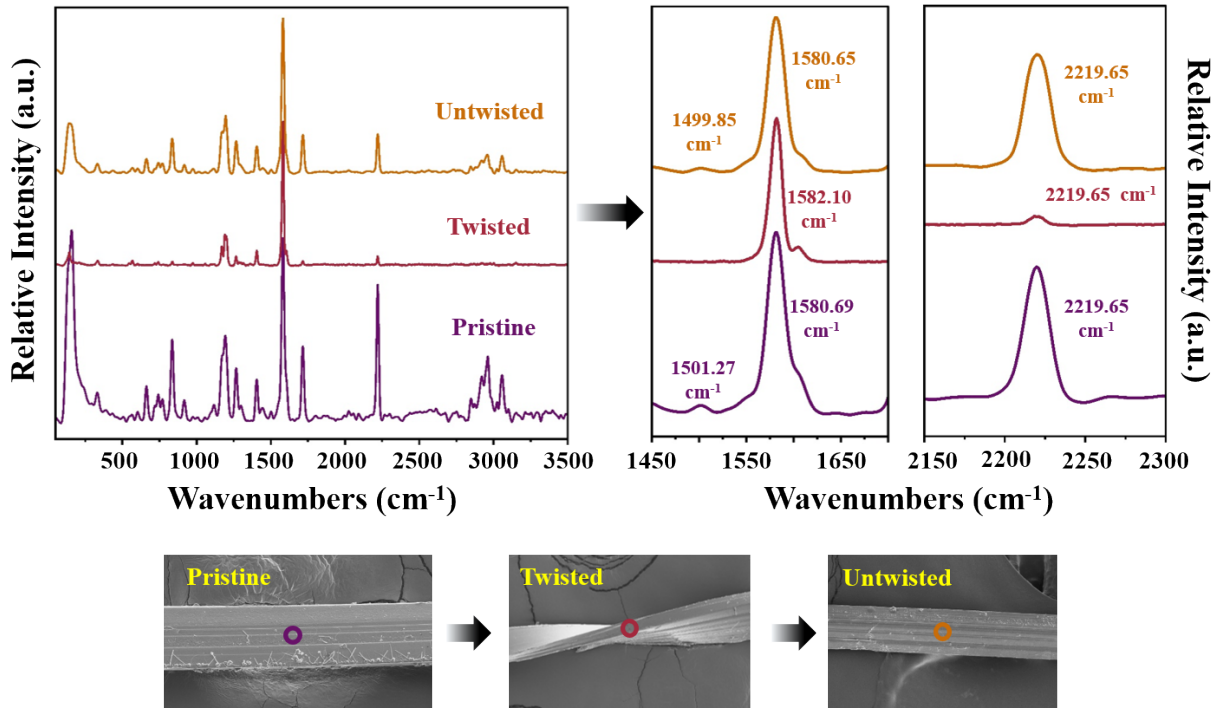


Fig. S9. Micro-focus Raman Spectra of Crystal **ECA**, pristine, twisted, and untwisted crystal.

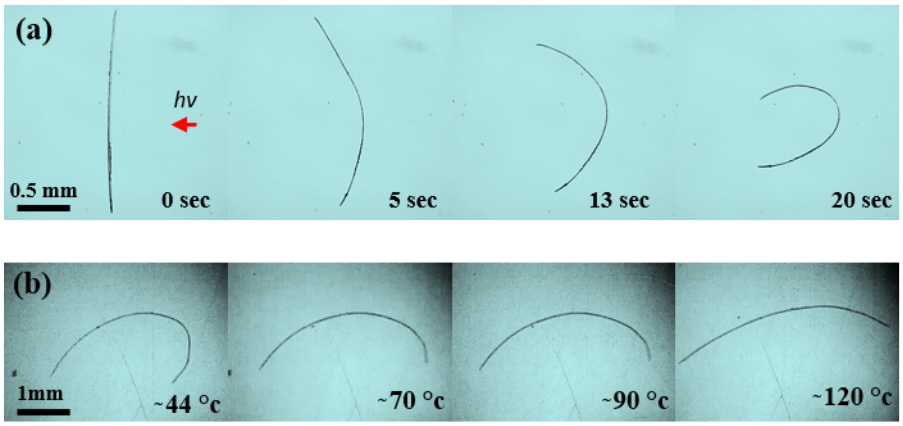


Fig. S10 (a) Stepwise photomechanical bending of crystal **ECA** and (b) Thermal reversibility of crystal **ECA** after photomechanical bending.

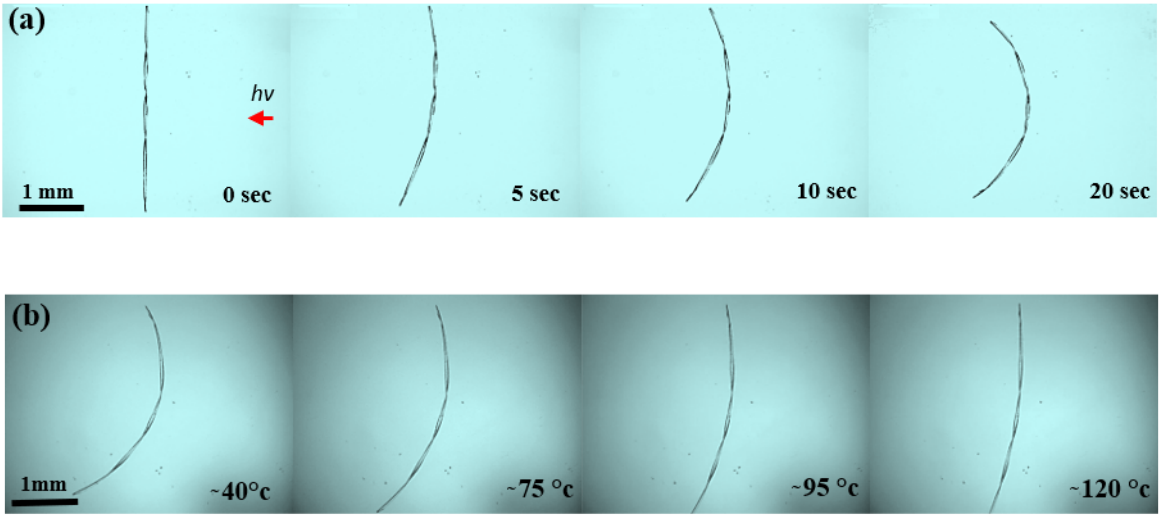


Fig. S11 (a) Stepwise photomechanical bending of twisted crystal **ECA** and (b) Thermal reversibility of twisted crystal **ECA** after photomechanical bending.

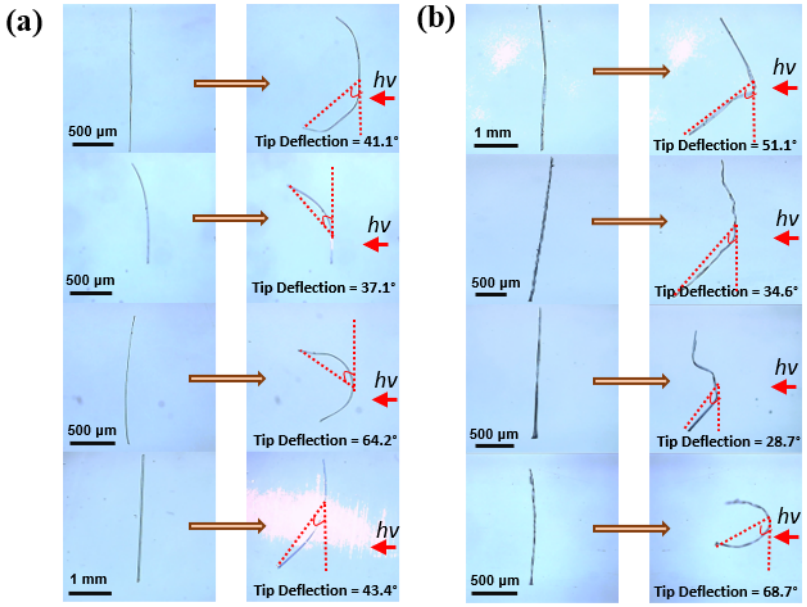


Fig. S12 (a) and (b) shows photomechanical bending of **ECA** crystals with varying dimensions before and after twisting.

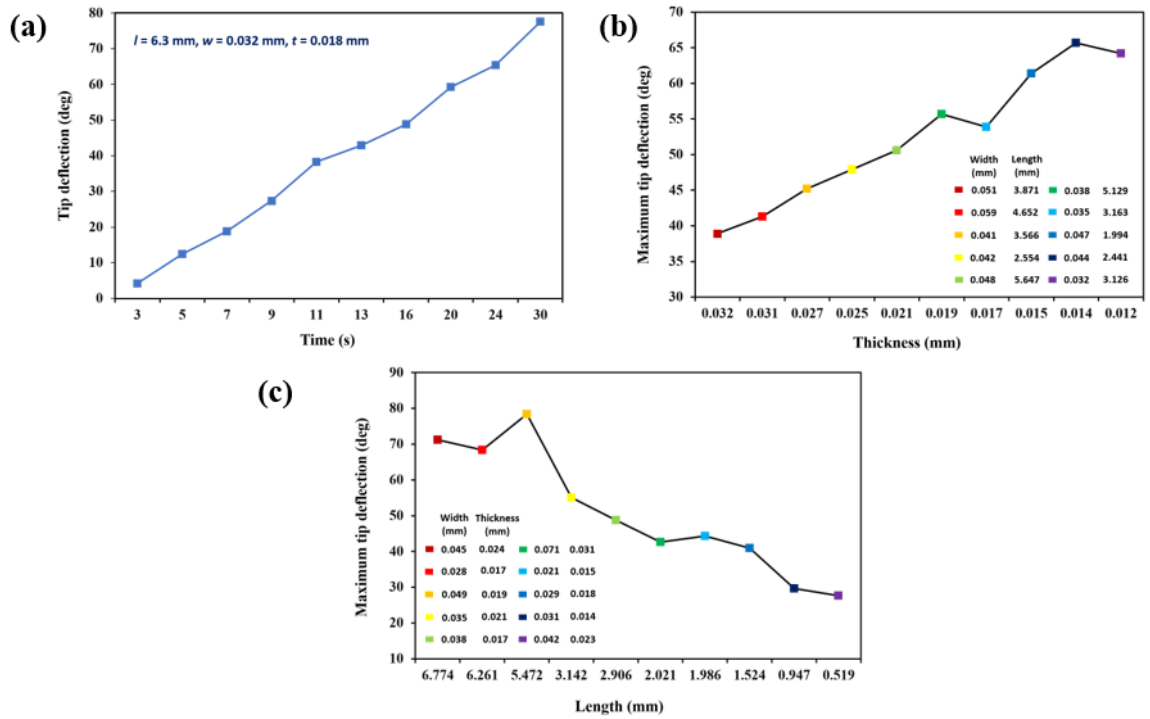


Fig. S13 Photomechanical bending in crystal **ECA** before twisting. (a) Plot of tip deflection vs time for crystal **ECA**, (b) plot of maximum tip deflection vs crystal thickness and (c) plot of maximum tip deflection vs crystal length.

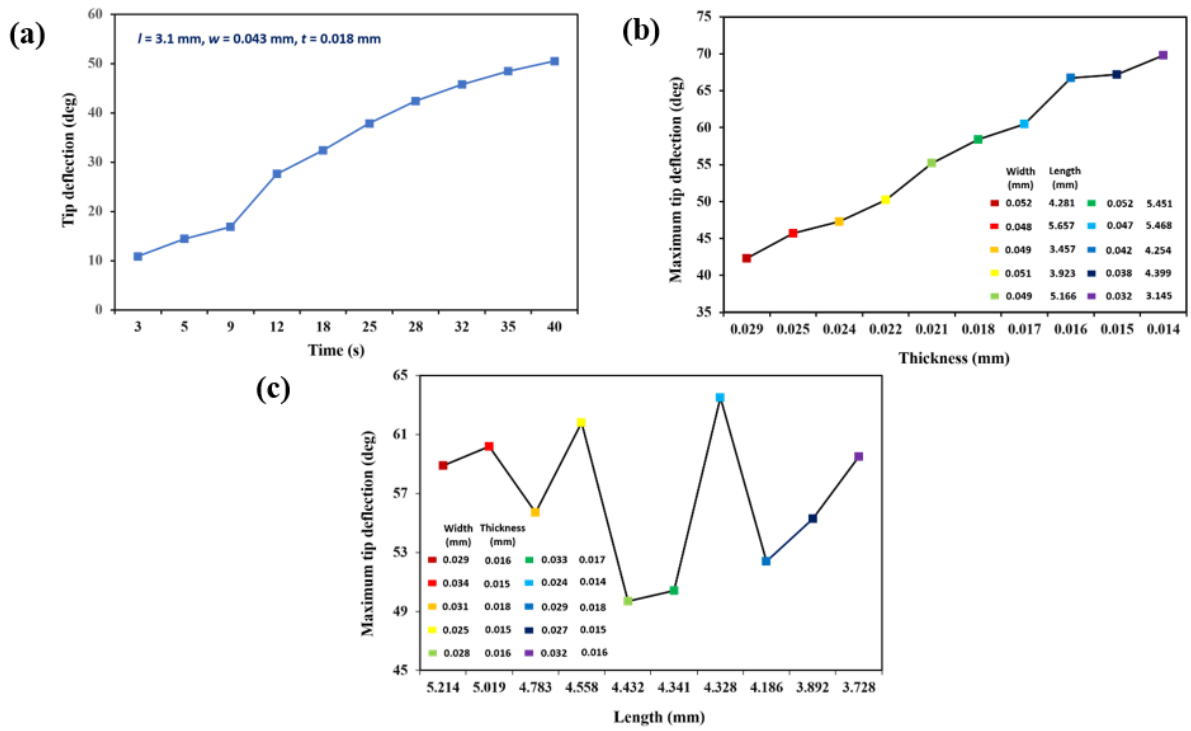


Fig. S14 Photomechanical bending in crystal **ECA** after twisting. (a) Plot of tip deflection vs time for crystal **ECA**, (b) plot of maximum tip deflection vs crystal thickness and (c) plot of maximum tip deflection vs crystal length.

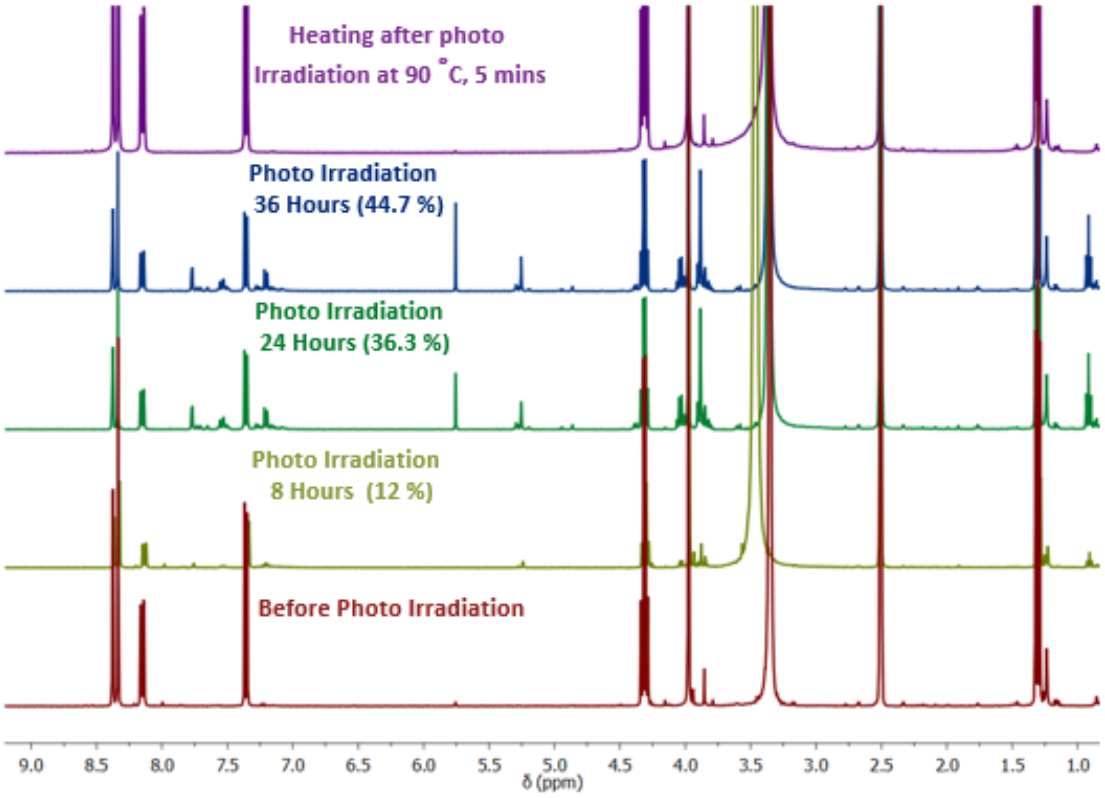


Fig. S15 ^{1}H NMR overlay diagram of crystal **ECA** depicting spectra of pristine sample, UV-irradiated sample with yield % (8 hours – 12 %, 24 hours – 36.3 %, 36 hours – 44.7 %) and heating after the irradiated bulk crystals were placed in a petri dish and heated at 90 °C for 5 minutes using a calibrated hot stage under ambient conditions.

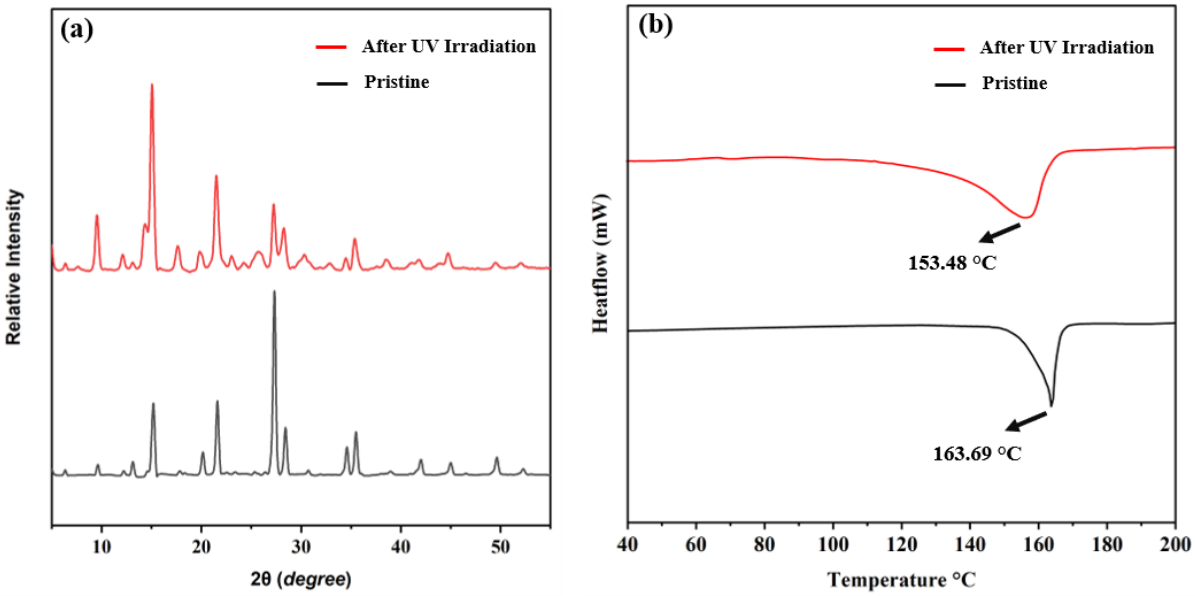
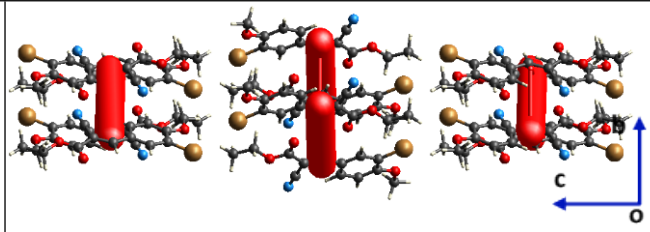
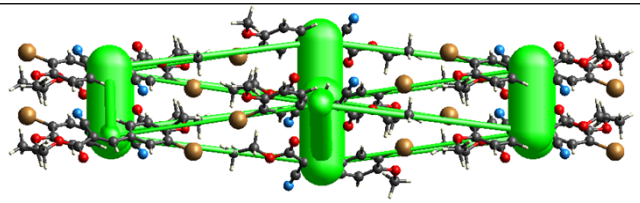
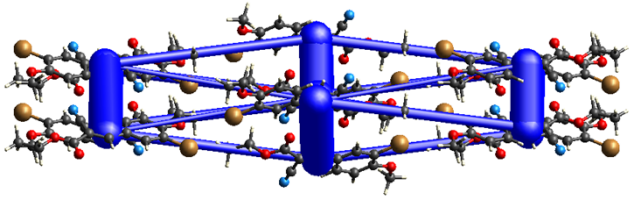
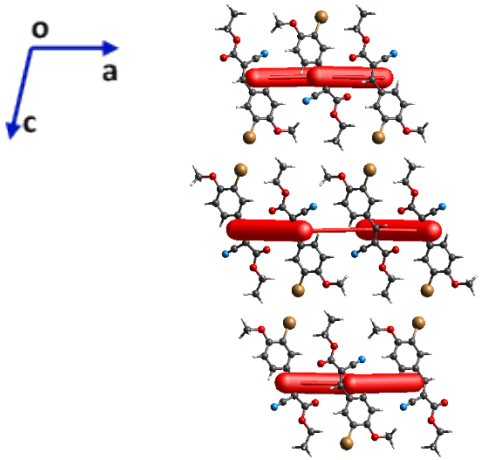
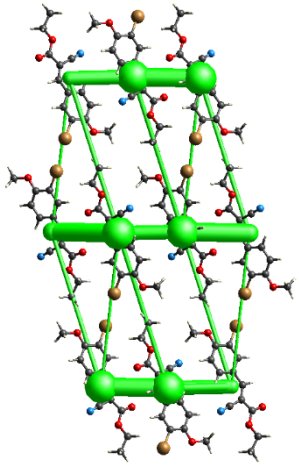
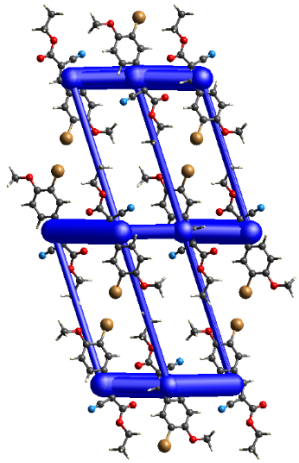
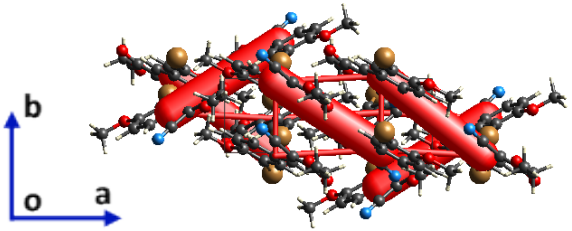
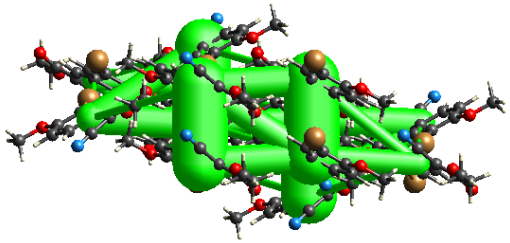
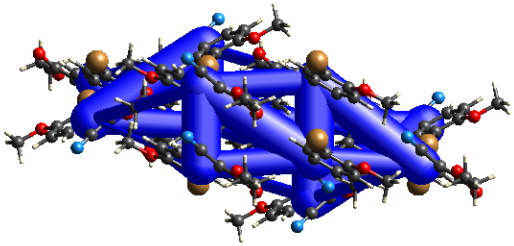
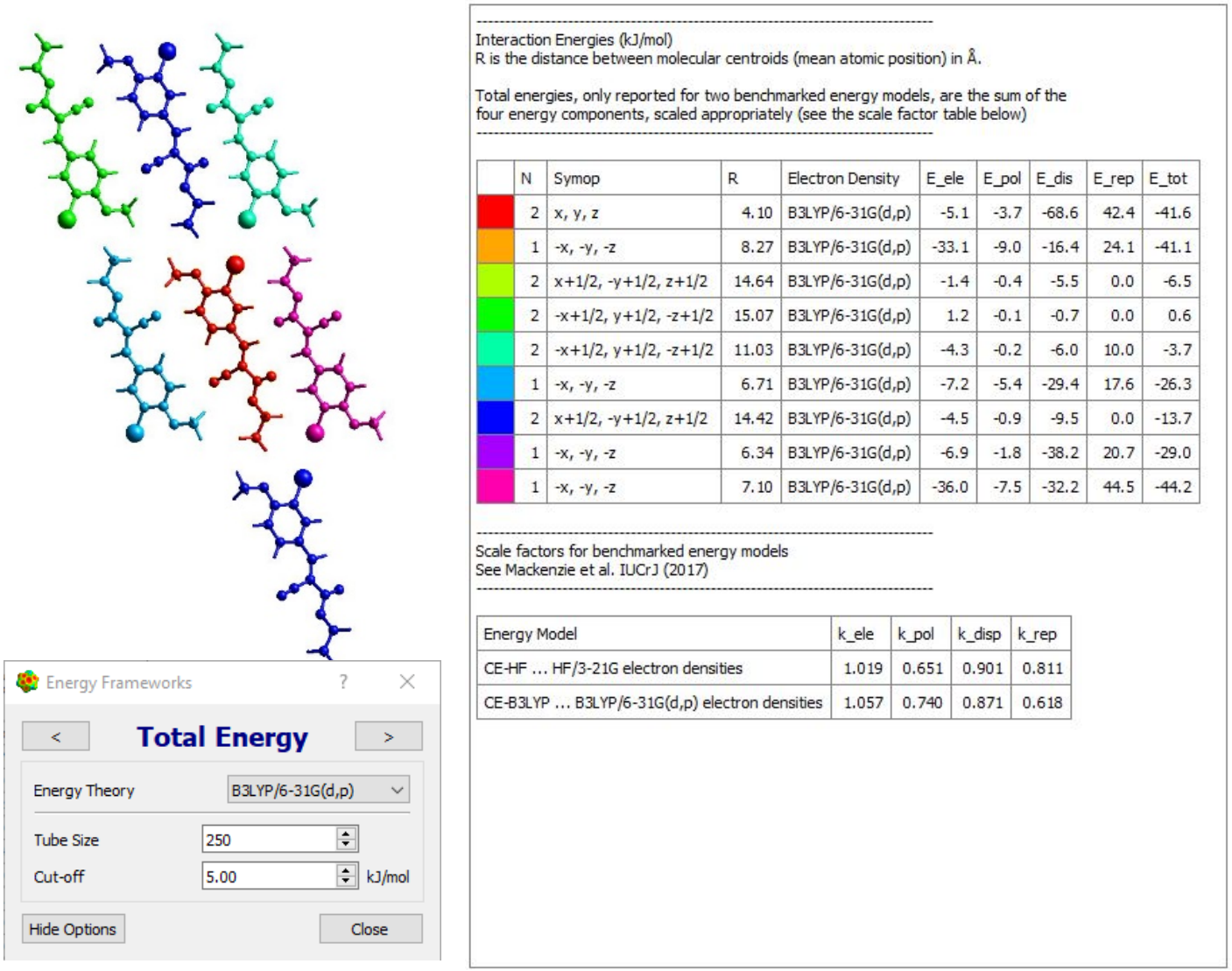


Fig. S16 (a) and (b) Shows PXRD and DSC profile of crystal **ECA** before and after irradiation.

	Electrostatic Interaction	Dispersion Interaction	Total Interaction
a-axis			
b-axis			
c-axis			



Interaction Energies (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x, y, z	4.10	B3LYP/6-31G(d,p)	-5.1	-3.7	-68.6	42.4	-41.6
	1	-x, -y, -z	8.27	B3LYP/6-31G(d,p)	-33.1	-9.0	-16.4	24.1	-41.1
	2	x+1/2, -y+1/2, z+1/2	14.64	B3LYP/6-31G(d,p)	-1.4	-0.4	-5.5	0.0	-6.5
	2	-x+1/2, y+1/2, -z+1/2	15.07	B3LYP/6-31G(d,p)	1.2	-0.1	-0.7	0.0	0.6
	2	-x+1/2, y+1/2, -z+1/2	11.03	B3LYP/6-31G(d,p)	-4.3	-0.2	-6.0	10.0	-3.7
	1	-x, -y, -z	6.71	B3LYP/6-31G(d,p)	-7.2	-5.4	-29.4	17.6	-26.3
	2	x+1/2, -y+1/2, z+1/2	14.42	B3LYP/6-31G(d,p)	-4.5	-0.9	-9.5	0.0	-13.7
	1	-x, -y, -z	6.34	B3LYP/6-31G(d,p)	-6.9	-1.8	-38.2	20.7	-29.0
	1	-x, -y, -z	7.10	B3LYP/6-31G(d,p)	-36.0	-7.5	-32.2	44.5	-44.2

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

Fig. S17. Energy Framework analysis of **ECA** Crystal.

References:

1. H. Yasuda and H. Midorikawa, *Bull. Chem. Soc. Jpn.,* 1966, **39**, 1754–1759.
2. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112–122.
3. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2015, **71**, 3–8.
4. A. Paikar, D. Podder, S. R. Chowdhury, S. Sasmala and D. Haldar. *CrystEngComm*, 2019, **21**, 589-593.